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SOLUBILITY OF CADMIUM SULFATE IN $\text{H}_2\text{O}-\text{D}_2\text{O}$ MIXTURES

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ABSTRACT

The work reported here is a continuation of earlier studies on the effect of heavy water on the electromotive force of standard cells.

The solubility of cadmium sulfate was measured in heavy water and in normal water. This salt was found to be about 8 percent less soluble in heavy water than in normal water in the temperature range -1° to $+70^\circ \text{C}$.

At 43.6°C , $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot \text{H}_2\text{O}$, and saturated H_2O solution are in equilibrium. $\text{CdSO}_4 \cdot 8/3\text{D}_2\text{O}$, $\text{CdSO}_4 \cdot \text{D}_2\text{O}$, and saturated D_2O solution are in equilibrium at 45.4°C .

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I. INTRODUCTION

The solubility of cadmium sulfate in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures was studied as a part of the work on standards of electromotive force dealing with the effect of D_2O on the electromotive force of standard cells. Two groups of cells described in earlier publications [1, 2]¹ have been made with mixtures of H_2O , HDO , and D_2O .

II. MEASUREMENTS

The solubility of cadmium sulfate was measured from -1° to $+72^\circ \text{C}$ in water that varied from 0.02 (normal water) to 99.5 mole percent D_2O . The experiments were made by continuously agitating crystals of cadmium sulfate in contact with the various aqueous solutions for periods varying from 24 to 300 hours. In most of the experiments 1- to 2-gram samples of the clear solution were removed for analysis. The CdSO_4 content was determined gravimetrically as CdSO_4 after heating the carefully dried sample in a muffle at 680° to 700°C in a stream of SO_3 gas. In a few experiments, those at 23.5°C , the composition of the saturated CdSO_4 solution was determined by

¹Figures in brackets indicate the literature references at the end of this paper.

synthesis. Weighed amounts of CdSO_4 were added to a known weight of water until only a very small amount of the crystals remained undissolved after being shaken with the solution for 24 hours or longer.

Because cadmium sulfate dissolves very slowly, considerable attention was given to the matter of obtaining saturated solutions. At each temperature the salt was agitated continuously with the solution for very long periods of time—usually from several days to a week or longer. Further, from some solutions a second sample was taken for analysis after an additional shaking period of 20 hours. In some cases two flasks with the same solvent with different proportions of crystals and solution were agitated simultaneously, and the solutions from each were analyzed.

The solubility measurements for the monohydrate, $\text{CdSO}_4 \cdot \text{H}_2\text{O}$, at 29° and 72° C were made in a different way from the measurements described above. The solutions were allowed to remain in contact with $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ crystals for 4 or 5 days and the flasks were shaken intermittently. The temperature varied by ± 2 degrees centigrade. These data are much less precise than the other data of this report. They are included, however, because they greatly extend the temperature range of the monohydrate solubility curve.

Many of the earlier measurements above 40° C have not been included in the results reported here because of the uncertainty of which crystal hydrate was in contact with the solution. Above 40° C the solutions were saturated in ampules in a water bath controlled to ± 0.05 degree because of the need of determining the hydrate transition temperature [3] and because of the greater change in solubility with temperature at the higher temperatures.

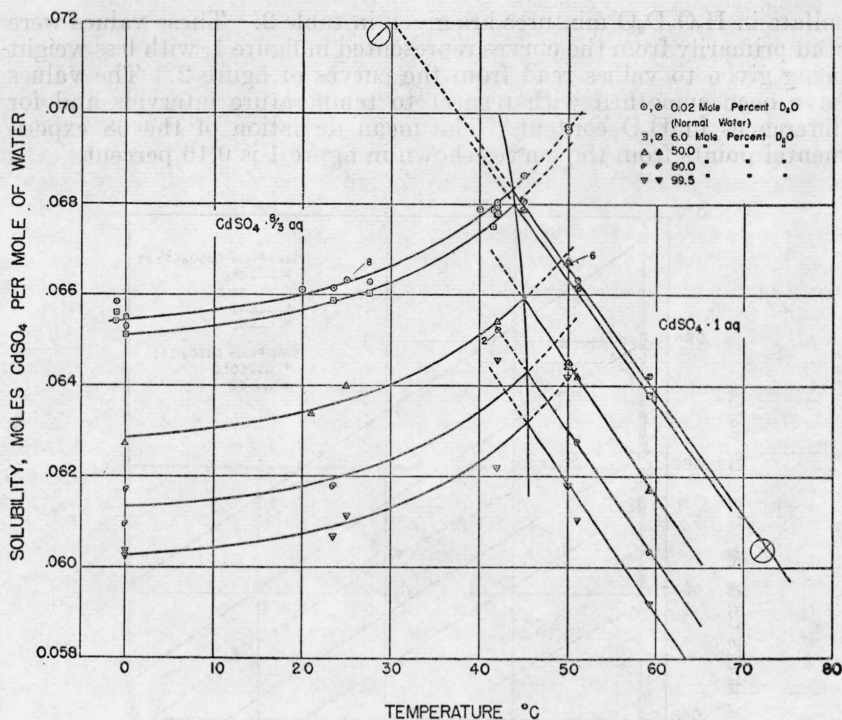
The deuterium content of the water was determined by density measurements after vacuum distillation of the samples. The volume was measured in a 0.4-milliliter pipette with calibrated inlet and outlet tubes. Weighings to ± 10 micrograms were made on a high-precision balance by transposing the pipette and tare. The total deuterium content was calculated as D_2O , and is expressed throughout as mole percent D_2O of the water, although HDO was of course present.

The solubility measurements are reported for waters containing 0.02, 6.0, 50.0, 80.0, and 99.5 mole percent D_2O . In cases where the D_2O content varied slightly from these values, the solubility values were adjusted for the differences and are given for the five D_2O concentrations listed here.

III. EXPERIMENTAL RESULTS

The experimentally determined solubilities of cadmium sulfate, expressed as moles of CdSO_4 per mole of water, in normal water (0.02 mole percent D_2O), 6.0, 50.0, 80.0, and 99.5 mole percent D_2O are shown in figure 1 as they vary from -1° to $+72^\circ$ C.

From -1° to $+43.6^\circ$ C the crystal phase in stable equilibrium with an H_2O solution of cadmium sulfate is $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. Above 43.6° the more stable crystal modification is $\text{CdSO}_4 \cdot \text{H}_2\text{O}$. The curves on the left in figure 1 represent the composition of solutions in equilibrium with $\text{CdSO}_4 \cdot 8/3\text{aq}$. The nearly parallel straight lines of the figure represent the composition of solutions in equilibrium with

FIGURE 1.—Solubility of cadmium sulfate in H_2O - D_2O mixtures.

Numerals indicate number of observations represented by a single point.

$\text{CdSO}_4 \cdot 1\text{aq}$. The equilibrium temperature for $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, $\text{CdSO}_4 \cdot \text{H}_2\text{O}$, and saturated H_2O solution is 43.6°C at atmospheric pressure. On the other hand, for $\text{CdSO}_4 \cdot 8/3\text{D}_2\text{O}$, $\text{CdSO}_4 \cdot \text{D}_2\text{O}$, and saturated D_2O solution the equilibrium temperature is 45.4°C . These equilibrium temperatures and those for mixtures of the hydrate and deuterate are given in table 1. The temperatures are those of the intersections of the two solubility curves for each H_2O - D_2O mixture. The compositions of the saturated solution in equilibrium with the two crystal modifications are also given in table 1.

TABLE 1.—Equilibrium temperatures for $\text{CdSO}_4 \cdot 8/3\text{aq}$, $\text{CdSO}_4 \cdot 1\text{aq}$, and saturated solution

| Composition of solvent, mole percent D_2O — | 0.02 | 6.0 | 50.0 | 80.0 | 99.5 | 100. |
|--|---------|---------|---------|---------|---------|---------|
| Equilibrium temperature, $^\circ\text{C}$ — | 43.6 | 43.9 | 45.0 | 45.3 | 45.4 | 45.4 |
| Composition of saturated solution, moles of CdSO_4 per mole of water— | 0.06833 | 0.06803 | 0.06592 | 0.06430 | 0.06317 | 0.06314 |

The experimentally determined solubilities plotted with respect to temperature, shown in figure 1, are also plotted as a function of the D_2O content of the solvent in figure 2. Thirty points which can be read from each set of curves agree very closely, the mean deviation being 0.06 percent. The best values for the solubilities of cadmium

sulfate in H_2O - D_2O mixtures are given in table 2. These values were read primarily from the curves represented in figure 1, with less weight being given to values read from the curves of figure 2. The values have been smoothed with respect to temperature intervals and for differences in D_2O content. The mean deviation of the 68 experimental points from the curves shown in figure 1 is 0.16 percent.

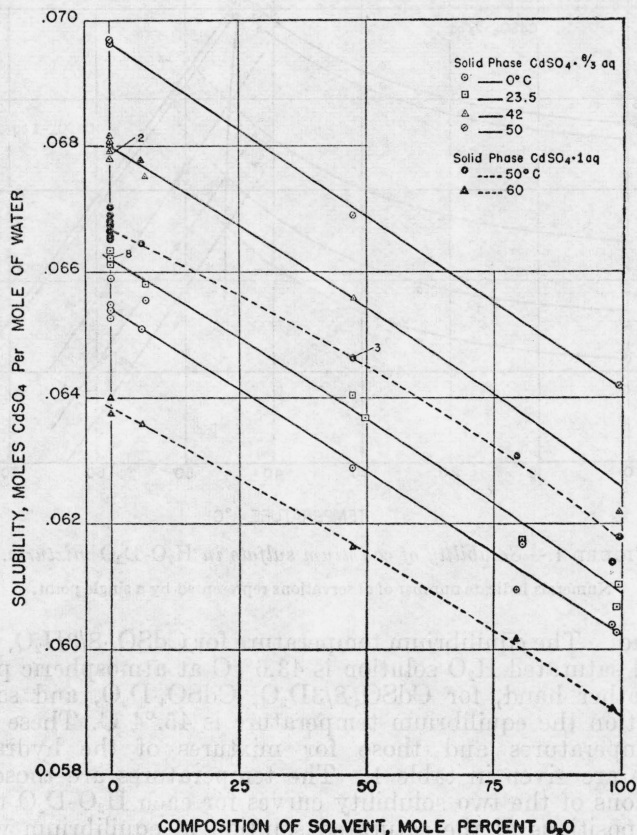


FIGURE 12.—Isothermal lines for the solubility of cadmium sulfate in mixtures of H_2O and D_2O .

Numerals indicate the number of observations represented by a single point.

The experimentally determined solubilities extrapolated to the solubility in 100 mole percent D_2O , designated as $S_{\text{D}_2\text{O}}$, are given in column 8 of table 2. The differences in solubility in H_2O and D_2O , $S_{\text{H}_2\text{O}} - S_{\text{D}_2\text{O}}$, are shown in column 9 and the percentage difference in column 10. The CdSO_4 content is about 8 percent less for $\text{CdSO}_4 \cdot \frac{8}{3} \text{D}_2\text{O}$ in D_2O than for $\text{CdSO}_4 \cdot \frac{8}{3} \text{H}_2\text{O}$ in H_2O . The CdSO_4 content is about 7.3 percent (6.9 percent at 45° and 7.7 percent at 60° C) less for $\text{CdSO}_4 \cdot \text{D}_2\text{O}$ in D_2O than for $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ in H_2O .

TABLE 2.—Solubility of cadmium sulfate in H_2O - D_2O mixtures[Moles of CdSO_4 per mole of water]

| Solid phase | Temperature ° C | Composition of solvent, mole percent D_2O | | | | | | Difference of solubility in H_2O and D_2O | |
|--|--------------------|---|---------|---------|---------|---------|---------|--|---|
| | | 0.02 | 6.0 | 50.0 | 80.0 | 99.5 | 100 | $S_{\text{H}_2\text{O}} - S_{\text{D}_2\text{O}}$ | $\frac{S_{\text{H}_2\text{O}} - S_{\text{D}_2\text{O}}}{S_{\text{H}_2\text{O}}} \times 100$ |
| $\text{CdSO}_4 \cdot 8/3\text{aq}$ ----- | 0 | 0.06546 | 0.06511 | 0.06285 | 0.06131 | 0.06029 | 0.06026 | 0.00520 | 7.94 |
| | 5 | 0.06555 | 0.06520 | 0.06294 | 0.06138 | 0.06036 | 0.06033 | 0.00522 | 7.96 |
| | 10 | 0.06566 | 0.06531 | 0.06305 | 0.06147 | 0.06045 | 0.06042 | 0.00524 | 7.98 |
| | 15 | 0.06580 | 0.06545 | 0.06319 | 0.06159 | 0.06058 | 0.06055 | 0.00525 | 7.98 |
| | 20 | 0.06600 | 0.06565 | 0.06339 | 0.06177 | 0.06076 | 0.06073 | 0.00527 | 7.99 |
| | 23.5 | 0.06619 | 0.06584 | 0.06358 | 0.06194 | 0.06093 | 0.06090 | 0.00529 | 7.99 |
| | 25 | 0.06627 | 0.06592 | 0.06366 | 0.06202 | 0.06100 | 0.06097 | 0.00530 | 7.99 |
| | 30 | 0.06663 | 0.06627 | 0.06402 | 0.06236 | 0.06133 | 0.06130 | 0.00533 | 7.99 |
| | 35 | 0.06710 | 0.06674 | 0.06449 | 0.06281 | 0.06177 | 0.06174 | 0.00536 | 7.99 |
| | 40 | 0.06773 | 0.06737 | 0.06512 | 0.06342 | 0.06235 | 0.06232 | 0.00541 | 7.99 |
| | 42 | 0.06803 | 0.06769 | 0.06542 | 0.06371 | 0.06263 | 0.06260 | 0.00543 | 7.98 |
| | 45 | 0.06857 | 0.06823 | 0.06594 | 0.06423 | 0.06314 | 0.06311 | 0.00546 | 7.96 |
| | 50 | 0.06966 | 0.06932 | 0.06696 | 0.06530 | 0.06418 | 0.06415 | 0.00551 | 7.91 |
| | 45 | 0.06797 | 0.06775 | 0.06591 | 0.06440 | 0.06330 | 0.06326 | 0.00471 | 6.93 |
| | 50 | 0.06659 | 0.06638 | 0.06448 | 0.06299 | 0.06185 | 0.06181 | 0.00478 | 7.18 |
| $\text{CdSO}_4 \cdot 1\text{aq}$ ----- | 55 | 0.06522 | 0.06501 | 0.06304 | 0.06159 | 0.06041 | 0.06037 | 0.00485 | 7.44 |
| | 60 | 0.06385 | 0.06363 | 0.06159 | 0.06019 | 0.05897 | 0.05893 | 0.00492 | 7.71 |
| | 65 | 0.0624 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | 70 | 0.0611 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| | 72 | 0.0605 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |

^a $S_{\text{H}_2\text{O}}$ denotes the solubility of cadmium sulfate in 100 percent of H_2O or in normal H_2O (0.02 percent D_2O).

^b $S_{\text{D}_2\text{O}}$ denotes the solubility in 100 percent D_2O .

IV. COMPARISON WITH OTHER DATA IN THE LITERATURE

No other data were found in the literature for the solubility of cadmium sulfate in D_2O . The solubilities of several other salts in D_2O have been reported, and these data are summarized in table 3. Except for SrCl_2 , the difference in solubility in H_2O and D_2O of the other salts is of the same order of magnitude as for CdSO_4 in the temperature range of the present work.

TABLE 3.—Comparison of solubility of CdSO_4 and some other salts in H_2O and D_2O

| Solid phase | Solubility in H_2O , $S_{\text{H}_2\text{O}}$ | $\frac{S_{\text{H}_2\text{O}} - S_{\text{D}_2\text{O}}}{S_{\text{H}_2\text{O}}} \times 100$ | Temperature ° C | Authors |
|---|--|---|--------------------|--------------------------------|
| | <i>Moles anhydrous salt per mole H_2O</i> | <i>Percent</i> | | |
| $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ ----- | { 0.06543 | 7.94 | 0 | National Bureau of Standards. |
| | { 0.06768 | 7.99 | 40 | Do. |
| $\text{CdSO}_4 \cdot \text{H}_2\text{O}$ ----- | { 0.06797 | 6.93 | 45 | Do. |
| | { 0.06385 | 7.71 | 60 | Do. |
| $\text{CuSO}_4 \cdot 5\text{aq}$ ----- | { 0.0173 | 13 | 5 | Miles and Menzies [4]. |
| | { 0.0324 | 5.0 | 40 | Do. |
| $\text{CuSO}_4 \cdot 3\text{aq}$ ----- | { 0.0847 | 1.7 | 95 | Do. |
| | { 0.0868 | 1.0 | 100 | Do. |
| $\text{SrCl}_2 \cdot 6\text{aq}$ ----- | { 0.0502 | 0.4 | 0 | Do. |
| | { 0.0738 | -1.7 | 40 | Do. |
| | { 0.0891 | -3.8 | 55 | Do. |
| $\text{SrCl}_2 \cdot 2\text{aq}$ ----- | { 0.1001 | 2.0 | 65 | Do. |
| $\text{SrCl}_2 \cdot \text{aq}$ ----- | { 0.1338 | -0.3 | 125 | Do. |
| | { 0.1455 | 3.2 | 135 | Do. |
| KCl ----- | { 0.0680 | 16.4 | 0 | Shearman and Menzies [5]. |
| | { 0.0967 | 6.7 | 40 | Do. |
| BaCl_2 ----- | { 0.1723 | 1.8 | 160 | Do. |
| | { 0.0309 | 11.8 | 20 | Taylor, Caley, and Eyring [6]. |
| NaCl ----- | { 0.111 | 7.8 | 25 | Do. |
| | { 0.1107 | 5.4 | 25 | Chang and Chu [7]. |

Chang and Chu [7] worked with NaCl in eight water mixtures from 0.02 to 99.59 mole percent D₂O. They found that the solubility of NaCl at 25° C decreased linearly with the increase in D₂O content of the water. Our data for CdSO₄ show that only at 0° and 50° C does a strictly linear relation hold. At the other temperatures in this investigation, 23.5° to 60° C, the curves are slightly concave downward (fig. 2).

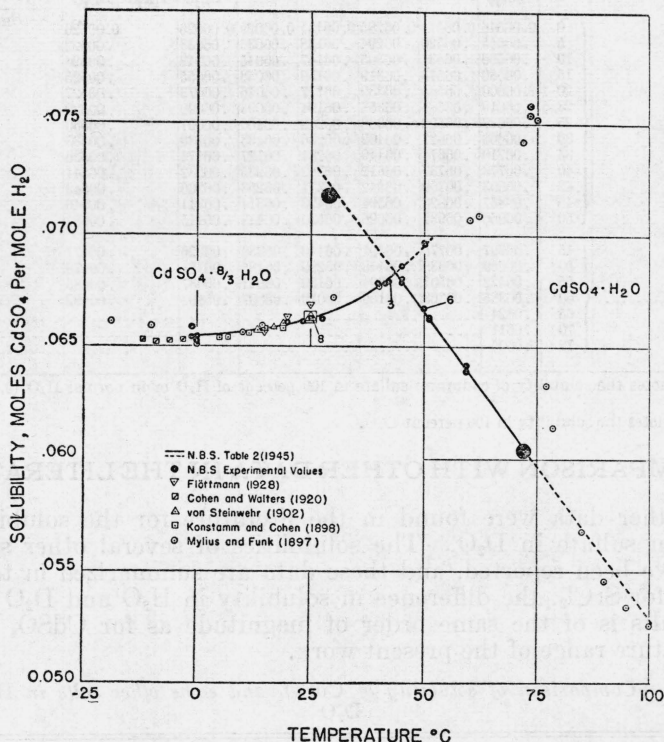


FIGURE 3.—Solubility of cadmium sulfate in H₂O as given in the literature and from NBS measurements.

The solubility of CdSO₄ in H₂O has been measured by a number of workers [8, 9, 10, 11, and 12]. Some of these determinations and the values reported here are represented in figure 3. The curves represent our best values for the solubility in H₂O as given in table 2. Below 40° C they are in good agreement with many of the earlier measurements. Because the earlier experimenters did not recognize the fact that the transition from the 8/3 hydrate modification to the monohydrate crystal occurred as low as 43.6° C and were working with the salt in a metastable condition, the earlier work deviates sharply from the values reported here at the higher temperatures. The occurrence of the transition between 43° and 44° C has been reported earlier [3]. In the earlier report, the equilibrium temperature for the two hydrates and the saturated solution was given as 43.4° C. The more extensive measurements reported here indicate that 43.6° is probably

a better value. The solubility data given in table 2 of this paper are also based on more extensive data than the values of the earlier report, from which they differ slightly.

V. SUMMARY

The solubility of cadmium sulfate in H_2O - D_2O mixtures varying from 0.02 to 99.5 mole percent D_2O has been determined over the temperature range -1° to $+72^\circ$ C. Values for the solubility of $\text{CdSO}_4 \cdot 8/3\text{aq}$ and $\text{CdSO}_4 \cdot 1\text{aq}$ are given for the various H_2O - D_2O mixtures. The CdSO_4 content of saturated solutions is about 8 percent less in D_2O than in H_2O .

The equilibrium temperature for $\text{CdSO}_4 \cdot 8/3\text{aq}$, $\text{CdSO}_4 \cdot 1\text{aq}$, and the saturated solution has been determined from the intersection of the solubility curves for the two crystal modifications. The equilibrium temperatures are 43.6° and 45.4° for H_2O and D_2O solvents, respectively.

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